**ESI for**

**Pressure-dependent guest binding and release on a supramolecular polymer**

1. General methods

Absorption spectra in solution were studied with a JASCO V-670 spectrophotometer. Fluorescence spectra were measured with a spectrofluorometer (JASCO FP-8500). TEM measurements were performed by JEOL JEM-2200. Unstained specimens were prepared by dropping the sample solutions onto carbon-coated copper grids. All spectroscopic measurements under high pressure were performed using a custom-built high-pressure vessel. The apparatus was designed and manufactured by Syn-Corporation (Kyoto, Japan). A quartz inner cell (4 mm × 4 mm) is connected to a Kalrez® tube, which is filled with a sample solution. The compression of this tube part adjusts the volume change of sample solution under pressurization. The inner cell with the Kalrez® tube was put inside the high pressure cell, in which water was filled to apply the hydrostatic pressure. The pressure inside the high pressure cell was adjusted by a hand pump unit. Measurement and excitation were conducted through Sapphire windows.

2. Supplemental spectra

![Absorption spectra](image)

Fig. S1 Absorption spectra of (R)-1 in an MCH/chloroform (9:1) mixture at various concentrations.
**Fig. S2** (a) Absorption spectral change of (R)-I in an MCH/chloroform (9:1) mixture upon pressurization ([I] = 3.0 × 10^{-5} M). (b) Plots of absorbance maxima of π-π* and charge transfer bands.

**Fig. S3** (a) Absorption spectral change of an NDI-derivative in a MCH/chloroform (9:1) mixture upon pressurization. Concentration: 6.0 × 10^{-5} M. (b) Plots of absorbance maxima of π-π* and charge transfer bands.
Fig. S4 Plots of the relative emission intensity ($I_{PDI}/I_{NDI}$) as a function of pressure at various contents of guest (S)-3. [1] = 3.0 × 10^{-5} M.

Fig. S5 Fluorescence spectral change of (R)-1 in an MCH/chloroform (9:1) mixture upon pressurization. [1] = 3.0 × 10^{-5} M.
Fig. S6 (a) Fluorescence spectral change of (S)-1 in an MCH/chloroform (14:1) mixture in the presence of 2.5 mol% of (S)-2 upon pressurization. $[1] = 3.0 \times 10^{-5}$, $[2] = 7.5 \times 10^{-7}$ M, $\lambda_{ex} = 410$ nm. Inset: schematic illustration of (S)-1–(S)-2 coassembly. b) The relative emission intensity $(I_{\text{PDI}}/I_{\text{NDI}})$ as a function of pressure.

Fig. S7 (a) Absorption and (b) fluorescence spectral changes of (R)-1/(S)-3 (100:2.5) an MCH/chloroform (9:1) mixture at ambient pressure before and after the pressurization (400 MPa). $[1] = 3.0 \times 10^{-5}$ M, $[3] = 7.5 \times 10^{-7}$ M.
3. TEM measurement

Fig. S8 TEM images of (a,b) (R)-1 and (c,d) (R)-1/(S)-3 (100:2.5) assembly (a,c) before pressurization and (b,d) after pressurization-depressurization procedure (Scale bar: 100 nm).
4. Fluorescence anisotropy

For the evaluation of binding affinity of guest molecules towards the host-nanofibers 1, polarized fluorescence emissions at the peak positions with polarized excitations at 530 nm were analyzed for anisotropy. Four parameters based on the emission intensity ($I_{VV}$, $I_{VH}$, $I_{HV}$, and $I_{HH}$) were measured, where $I_{NM}$ corresponds to fluorescence intensity and N and M correspond to the angle ($V$: vertical, $H$: horizontal) of polarization for excitation and emission, respectively, and anisotropy ($g$) was obtained by the following equations.

$$G = \frac{I_{HV}}{I_{HH}} \quad (1)$$

$$\gamma = \frac{I_{VV} - G I_{VH}}{I_{VV} + 2GI_{VH}} \quad (2)$$

![Fluorescence anisotropy graph](image1)

Fig. S9 Fluorescence anisotropy ($r$) change of a standard dye (9,10-diphenylanthracene) in an MCH/chloroform (9:1) mixture upon pressurization. Concentration: $7.5 \times 10^{-5}$ M

![Fluorescence anisotropy graph](image2)

Fig. S10 Fluorescence anisotropy ($r$) change of (R)-3 in an MCH/chloroform (9:1) mixture upon pressurization. Concentration: $7.5 \times 10^{-7}$ M
5. Temperature dependent behavior

![Fluorescence spectral change](image1)

Fig. S11 (a) Fluorescence spectral change of (R)-1 in an MCH/chloroform (9:1) mixture in the presence of 2.5 mol% of (S)-3 with changing temperature. [1] = 3.0 × 10^{-5}, [3] = 7.5 × 10^{-7} M. (b) The relative emission intensity (I_{PDI}/I_{NDI}) as a function of temperature.

![Absorption spectral change](image2)

Fig. S12 (a) Absorption spectral change of (R)-1 in an MCH/chloroform (9:1) mixture in the presence of 2.5 mol% of (S)-3 with changing temperature. [1] = 3.0 × 10^{-5}, [3] = 7.5 × 10^{-7} M. (b) Plot of absorbance at 360 nm as a function of temperature.

The temperature decrease from 20 °C led to the decrease of sensitized emission of (S)-3 along with the recovery of fluorescence in (R)-1 (Fig. S11). The cooling of solution should result in the reinforcement of self-association of 1, releasing the guest 3. Meanwhile, the decrease of sensitized emission of (S)-3 was also observed upon heating above 30 °C, at which self-assembling structure of (R)-1 is maintained (Fig. S12). This result suggests that the host-guest cross-species association interactions are weaker than the same-species homo self-association assembly of (R)-1 as suggested by the pressure-dependent study.

References